

Report for 2004IN155B: Hydrologic and land use control on the nature and cycling of allochthonous of organic carbon in mixed land use water sheds within Central Indiana

- Other Publications:

- Crooker, K., Filley, T.R., Frey J., and Six, J. A comparison of molecular and isotopic chemistry of overland flow DOM and POM to soil sources. American Geophysical Union Fall 2004 Meeting.

Report Follows

Annual Report: Filley

Title: Hydrologic and land use control on the nature and cycling of allochthonous of organic carbon in mixed land use water sheds within Central Indiana :

Focus categories: ECL, AG, GEOCHE, HYDGEO

1. PROBLEM AND RESEARCH OBJECTIVES,

The control of short-lived hydrologic events (e.g. snow melt, storms) and land use (e.g. row crop agriculture) on the nature (source, structure) and reactivity (chemical, biological) of allochthonous organic matter (AOM) transferred to streams is poorly understood yet it is of critical importance in understanding a wide range of issues including surface water quality, general aquatic ecosystem function, coastal hypoxia, and even global carbon budgets. The ambiguity concerning the biogeochemical cycling of AOM is a function of many factors including the inherent chemical complexity of aquatic organic matter pools, poor temporal sampling resolution, and a lack of application of sophisticated biogeochemical techniques to the study. The goal of this investigation is to perform a detailed assessment of how the nature of soil organic matter and the frequency and intensity of hydrologic pulses control the quantity, source, and size distribution of AOM in mid sized and small agricultural water sheds in Central Indiana that ultimately discharge to the main stem of the Wabash River. This study will integrate both laboratory and field components combining a detailed molecular, isotopic and physical fractionation of soils and AOM from streams and tile drains.

2. METHODOLOGY AND PRINCIPAL FINDINGS

2.1. Methodology:

a. Sampling sites. Samples of allochthonous organic matter in water and soil organic material were collected, as described below, over the course of two consecutive growing seasons that alternate between conventional tillage and non-tilled agriculture at a field scale study, 2.4 mi², in the Sugar Creek basin at Leary-Weber Ditch (LWD). This site represents an existing collaboration with the United States Geologic Survey-Water Resources Division USGS-WRD (contact person Dr. Jeffery Frey, Indianapolis USGS Office). Additionally, event-based sampling was performed at Big Pine Creek Watershed, Warren County at Williamsport located at the bridge where Moore's Hill Road (CR 125 E) crosses the creek.

b. Aggregate SOC fractionation. Six paired soil samples were acquired in the spring of 2004 at discrete distances from the overland flow water-sampling weir at Leary Weber Ditch. Each sample was first separated into two layers (0-5cm) and (5-15cm) and fractionated into three different size classes. The physical fractionation scheme that was used is a recently developed method for isolating four functional C pools: (1) the non-protected particulate organic matter (POM) not occluded within microaggregates, (2) the microaggregate protected POM, (3) the silt and clay protected C, and (4) the biochemically protected pool or non-hydrolyzable silt and clay associated C. Coarse POM, microaggregates, and silt + clay C will be isolated from air-dried and sieved (2 mm) soil. These fractions were isolated as described by Six *et al.*, (2000)

c. AOM Isolation: AOM was isolated from overland flow sites, watershed creek sampling stations, and select tile drains in LWD and the stream station at BPC and fractionated into size or molecular weight ranges using convention filtration and hollow fiber ultrafiltration (Marley *et al.*, 1994; Guo *et al.*, 2000). We will collected fine particulate organic matter (FPOM), colloids and high molecular weight DOM (HWDOM), and low molecular weight DOM (LDOM) using glass

fiber filters (GF/F nominally 0.7 mm), 0.2 micron filters, and 1000 Da nominal cut off filters, respectively. The isolations were performed in the field or in the lab of the PI Tim Filley. Sampling was targeted to rainfall events that generated overland flow or ditch flow.

c. Biopolymer (molecular and isotopic) analysis of soil and AOM fractions: A molecular-level chemical degradation scheme designed to isolate the low molecular weight fragments of the refractory biomolecules was employed to track carbon source and cycling in soils and AOM fractions. Thus far most samples have been chemically analyzed using alkaline copper oxide oxidation in order to discriminate between C₃ and C₄ lignin and wax components of the aggregate and aquatic fractions. Lignin phenols were quantified by analysis of the trimethylsilane (TMS) derivatives of eight lignin phenol monomers (vanillin, acetovanillone, syringaldehyde, vanillic acid, acetosyringone, syringic acid, *p*-hydroxycinnamic acid, and ferulic acid) using a 5 point calibration curve for each of the target compounds relative to the IRS ethyl vanillin. The trimethylsilane (TMS) derivatives of nine hydroxy fatty acids and fatty di-acids were analyzed based upon target and proxy standards relative to the IRS of DL-12, hydroxystearic acid in a five-point calibration curve using extracted ion profiles. Total cutin and suberin acids are defined here as the sum of 16-hydroxyhexadecanoic acid, hexadecanoic diacid, 18-hydroxyoctadec-9enoic acid, and semiquantitation of 9,16&10,16 dihydroxyhexadecanoic acid, 9-octadecene1,18dioic acid, 7&8 hydroxyhexadecane dioic, 9,10,18 trihydroxyoctadec12enoic, and 9,10,18-trihydroxyoctanoic acid. A Shimadzu QP5050A quadrupole mass spectrometer interfaced to a GC17a gas chromatograph was used to identify and quantify selected mass fragments of the IRS and target compounds. Successful TMS derivatization of samples and GC/MS instrument performance was verified with a methyl 3,4-dimethoxybenzoate recovery standard which was added prior to derivatization of all samples and blanks.

The lignin analyses provide information on the oxidation state of the lignin compounds and the nature of the plant inputs to the soil. For example, information about the oxidation state of lignin can be inferred from the relative abundance of vanillic acid to vanillin (Ac/Al)_v and syringic acid to syringaldehyde (Ac/Al)_s, as microbial degradation of lignin increases the ratio of carboxylic acids to aldehydes. Additionally, the nature of plant inputs to the soil can be inferred by comparing the yield of syringyl or cinnamyl compounds normalized to yield of vanillyl compounds (S/V and C/V, respectively) where a high C/V and S/V is found for corn residues while a low C/V and high S/V is found for soy residues.

2. PRINCIPAL FINDINGS

Thus far molecular analysis of lignin source, quantity, and decomposition state have been completed on almost all of the LWD samples. The BPC analyses have yet to begin. We still await stable carbon isotope analyses on the sample. We anticipate these being completed by the end of July.

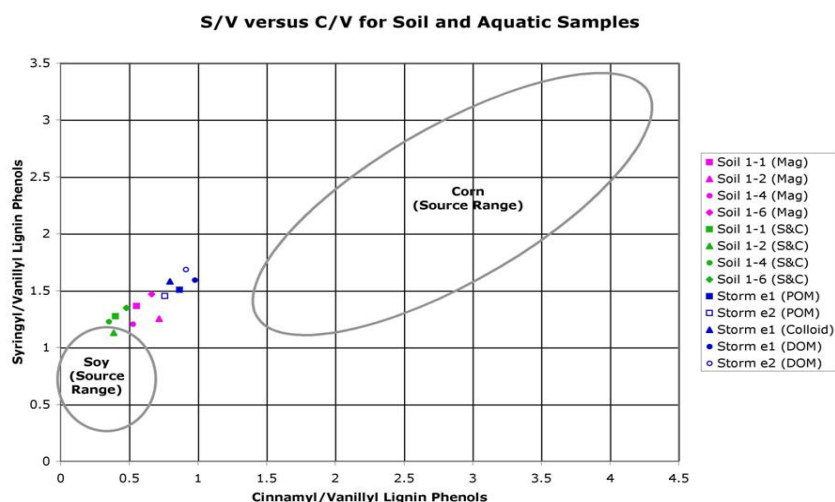


Figure 1. source proxy plot for LWD soil and aquatic fractions

Figure 1 shows the S/V and C/V source proxy plots for samples from LWD. By this graphical presentation we can investigate the sources of plant components in the two component system (soy and corn) to the soil, overland flow, and aquatic fractions. The silt and clay (S+C) and microaggregate fractions each plot near the soy residue suggesting that mineral associated organic matter and microaggregated SOM have an abundance of soy residues (most likely roots) associated with them. In contrast the storm flow aquatic fractions (dissolved organic matter-DOM, particulate organic matter -POM) plot further toward the corn residues suggesting that storm flow mobilizes corn stover at the surface rather than silts and clays of the soil.

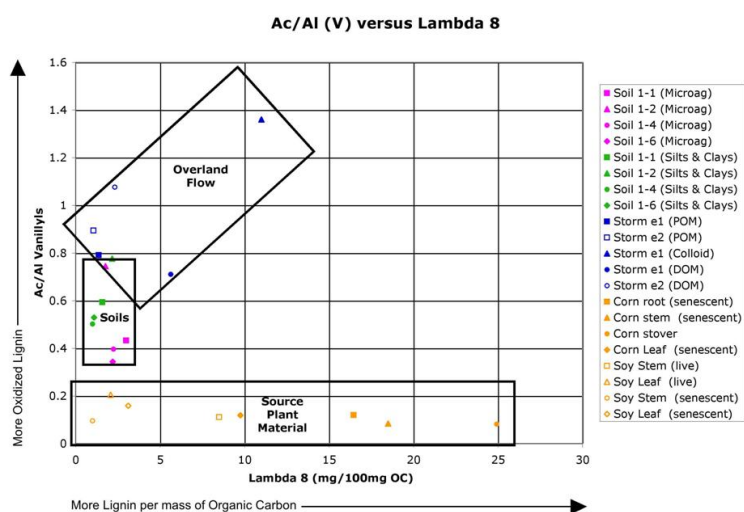


Figure 2. Plot of lignin yield and oxidation state for all fractions collected at LWD.

For the two storm events studied thus far the soil organic matter has significantly less lignin than most of the plant starting materials indicating progressive oxidation. Additionally,

overland flow exhibits elevated Ac/Al and a bit low to moderate lignin yields. Overland flow colloids appear to be selectively enriched in lignin above other size fractions from the events. Upon analysis of the stable carbon isotopes we should be able to determine what percentage the organic matter is of corn and soy and how hydrodynamic sorting acts to mobilize one over the other.

3. SIGNIFICANCE of the PROJECT

The export of AOM as dissolved, colloidal, or particulate forms has local to global significance as riverine carbon along with other coupled nutrients is both an important component of the global carbon cycle and also has important controls on water quality (e.g. THM production) and aquatic biology (e.g. hypoxia). For example, the net heterotrophic state of our land-use impacted rivers and streams may be a function of not just the quantity but also the forms and “reactivity” of AOM. It is unknown how much of this impact is inherited from the inherent reactivity or recalcitrance of the organic matter in the terrestrial plants or soils.

It is of local and national interest to be able to predict not just the quantity but also the reactivity and thus source of AOM exported to aquatic systems with the ultimate goal prediction of the fate of this carbon and co-mobilized nutrients or anthropogenic compounds. In fact, the rivers often provide the conduit for the co-mobilization of metals, pesticides, or other anthropogenic compounds that are bound or sorbed to AOM. These are issues that have been identified as being of high importance by the U.S. Global Change Research Program (USGCRP) as well as the NSF Water Cycles Research Program

4. STUDENTS,

This grant has funded in part the MS thesis for Mr. Keith Crooker, Department of Earth and Atmospheric Sciences (EAS). His anticipated graduation date in Dec 2005. This project also funded partially EAS undergraduate Megan Uttley.

5. THESIS TITLES, PAPERS, AND ABSTRACTS.

Poster Presentation . K. Crooker, Filley, T.R., Frey J., and Six, J. A comparison of molecular and isotopic chemistry of overland flow DOM and POM to soil sources. American Geophysical Union Fall 2004 Meeting.